REMARKS

Claims 1-21 were pending in the above-identified patent application. The title of the invention and the Specification have been amended for clarity. The amendments to Claims 20 and 21 are supported by the specification on page 6, lines 8 – 12 and on page 7, lines 25 - 28. No new matter or new issues are presented in the amendments. Based on the foregoing remarks, Applicants respectfully request reconsideration and allowance of the pending and new claims.

Applicants thank the Examiner for the courtesies extended during the interview of February 25, 2000.

Formal Matters

Applicants submit herewith certified translations of the priority documents, and are therefore entitled to the priority date of May 17, 1995.

The title has been changed to clearly indicate that the invention is directed to resin compositions containing a reducing agent to be used in a multi-laminate for storing liquid foods.

The specification has been modified as requested by the Examiner to clarify and correct minor errors. No new matter or new issues are contained in these amendments.

Rejections Under 35 U.S.C. § 112, first paragraph

The Amendment on page 2, line 20 was rejected under 35 U.S.C. §112, first paragraph, as containing subject matter not in the specification as originally filed. The Examiner states that the proposed amendment reads on a composition comprising an optional porous inorganic compound, whereas the originally filed specification required the inorganic compound be present. Applicants respectfully traverse this rejection.

The original specification, page 3, lines 1 – 8 describes two embodiments of the invention of the above-referenced application. One embodiment described on page 3, lines 4 – 8,

includes a porous inorganic compound. Since this is a component of only one of the two embodiments of the invention, and which are similar to each other in all other respects, inclusion of a porous inorganic compound is an optional feature, and therefore described as such in the Specification as originally filed. Applicants therefore respectfully request that this rejection be withdrawn.

The amendment on page 9, line 15, was rejected under 35 U.S.C. §112, first paragraph, as unclear as to the meaning of the phrase "filled together." The clause "or the composition can be wrapped by another appropriate compound and be filled together" has now been amended to clarify that the composition of the invention may be wrapped in another appropriate composition and this combination molded to form a container that may be filed with liquid food. Applicants therefore respectfully request that this rejection be withdrawn.

Claims 14 and 15 were rejected under 35 U.S.C. §112, first paragraph, for a lack of support in the Specification for the term "containing." In addition, amendments to the Specification were objected to as introducing new matter into the specification. Claims 14 and 15, and the Specification, are amended from having the term "containing", to having "supporting." Applicants therefore respectfully request that this rejection be withdrawn.

Rejection Under 35 U.S.C. § 112, second paragraph

Claims 1 and 3 were rejected under 35 U.S.C. 112, second paragraph, as indefinite for failing to particularly point out and distinctly claim the subject matter that Applicants regard as the invention. The Office Action indicates that the phrase "which is then" is indefinite, and it is unclear what part of the composition is dispersed in the hydrophobic thermoplastic resin. The Claims 1 and 3 have now been amended. The amendments to the claims clarify that it is the kneaded hydrophilic reducing organic compound and water insoluble thermoplastic resin composition that is dispersed in the hydrophobic thermoplastic resin. Therefore, Applicants respectfully request that the rejection be withdrawn.

Prior Art Rejections Under 35 U.S.C. § 103

As discussed in the interview, none of the cited references teach the unique concept of this invention that offers significant advantages over existing laminates and materials containing oxygen scavengers. No combination of the references teaches the protective function of the hydrophilic water insoluble thermoplastic resin that acts as the gas barrier. Cited references do not teach an advantage of the invention which is that the organic reducing agent is protected from oxygen until the hydrophilic layer is wetted by the aqueous food.

The Examiner rejected the argument presented by the Applicants in the Response mailed August 5, 1999 on the grounds that one of ordinary skill in the art would expect the oxygen absorbing characteristics of the hydrophilic reducing organic compound (component A) to increase when the resin composition of the present invention comes into contact with the aqueous food. (Office Action page 9, lines 6 – 9). The inclusion of the hydrophilic and water insoluble thermoplastic resin (component B), however, does not serve to diminish the oxygen absorbing characteristics of component A, which remain unaffected by the presence of the overlying component B. Instead, component B serves to protect and conserve the oxygen absorbing properties of the organic reducing agent (component A) until such time as oxygen can permeate the component B, when component B is wetted by the food. The protective function of the claimed structure is a unique advantage of the present invention not suggested by the cited references or any of their combinations.

The Examiner stated that one of ordinary skill in the art would know that the oxygen permeability of vinyl alcohol increases with its water content, citing references Torre et al., Markiewicz, and Akkapeddi et al. None of the cited references, however, alone or in combination, teach the novel use and advantage of the present invention, wherein the hydrophilic resin layer protects the organic reducing agent from deterioration before wetting.

The Examiner rejected Applicant's interpretation of "release" in the cited reference Daiichi Seiyaku. That the ascorbic acid in Daiichi Seiyaku is separated from the zeolite support is clearly expressed by the phrase "the chemical is release." "Release" means eliminated from the zeolite, i.e departs from the supporting material to which it is absorbed. This is in contrast to the present invention, wherein the ascorbate remains associated with the porous inorganic support within the hydrophilic resin, an advantage over the cited reference.

The present invention fulfills a long-felt need for an improved laminate for food storage that contains an organic reducing agent and a hydrophilic gas barrier activated by placing the food therein. The advantage of this unique combination is that the gas barrier is a hydrophilic layer that surrounds the organic reducing agent oxygen scavenger, thereby protecting the scavenger from oxygen and prolonging the effective life of the reducing agent. Once in contact with aqueous foods, the protective hydrophilic gas barrier is wetted and oxygen permeates to encounter the underlying organic reducing agent oxygen scavenger.

Thus, an important feature of the invention as indicated in the claims is that a hydrophilic reducing organic component (component A) is included in a hydrophilic and water insoluble thermoplastic resin (component B). In other words, the B component covers the A component. The A component is kneaded with the B component of the present invention. This process of kneading will allow the B component to surround the A component so that the A component is protected by the B component, which has oxygen gas barrier characteristics. This concept is schematically shown in the enclosed Fig. A. This feature is supported by the specification on page 6, lines 1 – 12, page 12, line 1 and on page 12, lines 7 – 8. Component A is prevented from being consumed by the surrounding oxygen before the resin composition contacts the aqueous liquid food. Therefore, component A maintains its oxygen absorbing capability. When the resin composition contacts the aqueous liquid food, the water component gradually reaches through the hydrophobic thermoplastic resin (component C) and decreases the oxygen

barrier characteristics of component B. As a result, the A component can then exhibit its oxygen absorbing function (page 12 lines 1 - 14). Applicants respectfully affirm that these above-mentioned features and advantages of Claims 1, 3, 20 and 21 are neither disclosed nor suggested in any references cited by the Examiner.

Another important feature of the invention according to Claims 14 and 15 is that a porous inorganic compound (D component) containing ascorbic acid (A component) is dispersed into hydrophobic thermoplastic resin (C component). In other words, this embodiment is the combination of the A/D component, the B component and the C component. An advantage of the above feature of the Claims 14 and 15 is that when the D component containing the A component is dispersed in the C component, the A component is uniformly dispersed in the C component. As a result, the oxygen absorbing function of the A component is improved in the C component. This is supported in the Specification on page 12, lines 8 – 10. It should also be noted that the ascorbic acids have a tendency to aggregate to form solids. Thus, if the ascorbic acids are dispersed in the C component without the support of the D component, the ascorbic acids will aggregate, and the rate of dispersion of the ascorbic acids in the resin and their capacity for oxygen are significantly reduced. This feature and advantage of the invention as claimed in Claims 14 and 15 are neither disclosed nor suggested in any references cited by the Examiner.

The utility of the present invention are well illustrated by the oxygen absorbing properties of the embodiments of the invention as disclosed in the application, Tables 1 and 2. Thus, Table 1 shows that the present invention has significant oxygen absorbing ability compared to control samples wherein the hydrophilic organic reducing compound is omitted. The examples in Table 2 show that the embodiments of the present invention, Table 2, embodiments 5 – 9, remain significantly active for at least 28 days and thereby maintain the oxygen content of the food at reduced levels compared to the Comparative Examples 2 and 3.

A. Claims 1, 3 and 5 - 8 were rejected under 35 U.S.C. § 103(a) as being obvious and unpatentable over Koyama et al. (Pat. No. 5,274,024) in view of Blinka et al. (Pat. No. 5,834,079). The priority date of the present application is May 17, 1995, derived from the foreign applications (Japan) P7-118430 and P7-118430. Verified translations of the priority documents supporting the priority date are attached. Applicants therefore respectfully request withdrawal of this rejection as moot.

B. The Examiner rejected Claims 12 and 13 under 35 U.S.C. § 103(a) as being unpatentable over Koyama et al. (Pat. No. 5,274,024) in view of Blinka et al. (Pat. No. 5,834,079) as applied in claims 1, 3 and 5 - 8 above, and further in view of Moritani et al. (Pat. No. 4,999,229). The priority date of the present application is May 17, 1995, derived from the foreign applications (Japan) P7-118430 and P7-118430. Verified translations of the priority documents supporting the priority date are attached. Applicants therefore respectfully request withdrawal of this rejection as moot.

C. Claims 1, 3 and 5 - 8 were also rejected as being unpatentable over Koyama et al. (Pat. No. 5,274,024) in view of JP-0172416 (assigned to Daiichi Seiyaku Co.) and Teumac et al. (Pat. No. 5,663,223). The Examiner indicates that it would have been obvious to one of ordinary skill in the art to incorporate the oxygen scavenger taught in Daiichi Seiyaku into the EVOH blend layer of the laminate taught in Koyama in order to enhance the oxygen barrier properties of the laminate. Applicants traverse the rejections as above and as follows.

Koyama merely discloses that the oxygen absorbing resin is a blend comprising a vinyl alcohol polymer and an olefin resin in a weight ratio of 1:99-90:10 (Claim 2), and an oxygen scavenger is incorporated in the blend (col. 6, lines 18-21). Daiichi Seiyaku merely discloses that an oxygen scavenger comprises a zeolite, either synthetic or natural, which supports one or more ascorbic or araboascorbic acids, their salts or derivatives thereof. The oxygen scavenger is apparently incorporated into the foodstuff that it is protecting. Teumac merely discloses that

oxygen scavengers which were once added directly to foodstuff are being incorporated into the food packing container (col. 3, lines 48+). None of the cited prior art teaches about following advantage to the present invention: the decrease in the oxygen barrier characteristics of component B and the protective effect this barrier has on the oxygen absorbing characteristics of component A, which is activated only when the resin composition of the present invention comes into contact with aqueous liquid foods. Therefore, the cited art does not provide the motivation to combine these elements to arrive at the present invention.

Applicants respectfully assert that one of ordinary skill in the art would not arrive at the present invention by combining the teachings of Koyama, Daiichi Seiyaku and Teumac. As indicated above, the present invention has many unique characteristics not taught by any prior art. Primarily, the kneaded hydrophilic organic reducing agent and hydrophilic water insoluble resin dispersed in a hydrophobic resin protects and conserves the oxygen absorbing properties until wetted with food. Thus, the objections to Claims 1 and 3, and dependent claims 5 - 8 should be withdrawn.

D. Claims 12, 13, 15 and 16 were rejected under 35 U.S.C. 103(a) as being unpatentable over Koyama et al. (Pat. No. 5,274,024) in view of JP-0172416 (assigned to Daiichi Seiyaku Co.) and Teumac et al. (Pat. No. 5,663,223) and further in view of Moritani et al. (Pat. No. 4,999,229). The Examiner states that it would have been obvious to one of ordinary skill in the art to utilize a polyolefin with a moisture permeability of not more than 20g/ml -day as the inner layer of the laminate taught in Koyama because Moritani teaches that laminates with such inner layers possess superior barrier properties. Applicants traverse the rejection as follows.

Koyama merely discloses that the oxygen absorbing resin is a blend comprising a vinyl alcohol polymer and an olefin resin in a weight ratio of 1:99-90:10 (Claim 2), and an oxygen scavenger is incorporated in the blend (col. 6, lines 18-21). Daiichi Seiyaku merely discloses than an oxygen scavenger comprises a zeolite, either synthetic or natural, which supports one or more

ascorbic or araboascorbic acids, their salts or derivatives thereof. The oxygen scavenger is apparently incorporated into the foodstuff that it is protecting. Teumac merely discloses that oxygen scavengers which were once added directly to foodstuff are being incorporated into the food packing container (col. 3, lines 48+). Moritani merely discloses a three-layer laminate, comprising an inner layer, an intermediate layer and an outer layer. The inner layer is selected from the group consisting of polyolefin, polyamides, and polyesters (col. 9, lines 21-45).

For the reasons already described above, Claims 12 and 13 which ultimately depend upon Claim 1, are for a resin composition used in a multi-layer laminate with several unique components. None of the cited prior art discloses an A component kneaded into a B component or that both these components undergo changes when the laminate comes into contact with liquid foods.

Claim 15 has been amended to indicate that the composition is directed to a laminate for packaging aqueous liquid foods. As indicated in the background (page 15 lines 3 - 13), an important and novel advantage of the invention is that the laminate for packing aqueous liquid foods comprises a layer made of resin that is prepared by dispersing a porous inorganic compound containing ascorbic acids into hydrophobic thermoplastic resin. The ascorbic acids in the resin layer are stable in the presence of oxygen under dry conditions and normal temperatures. So, it is possible to preserve the above-described function during the storage of the packaging material. However, when filled with aqueous liquid foods, the water component passes through the thermoplastic resin and gradually reaches the supporting porous inorganic compound, whereby the ascorbic acids exhibit an oxygen absorbing function. Therefore, it becomes possible to prevent any degradation of the liquid foods due to the presence of oxygen during storage. Thus, quality is preserved and shelf-life extended when aqueous liquid foods are packaged in a laminate comprising the present composition. Daiichi Seiyaku discloses porous inorganic compounds containing ascorbic acids. However, Daiichi Seiyaku assumes that ascorbic acids have to be

released from porous inorganic compounds to exhibit their oxygen absorbing capability. See attached copy of Japanese and English translation of portions of the same. When the porous inorganic compounds containing ascorbic acids as taught by Daiichi Seiyaku are incorporated in a hydrophobic thermoplastic resin, it is expected that the ascorbic acids would not be released from the porous inorganic compounds. Thus, when the ascorbic acids within the porous inorganic compounds are incorporated in the hydrophobic thermoplastic resin, it is expected that the ascorbic acids would not exhibit any oxygen absorbing capability. Therefore, Applicants believe that another novel feature of the present invention is the incorporation of ascorbic acids into porous inorganic compounds as described on page 13 lines 3-18. The above mentioned features of Claim 15 are neither disclosed nor suggested in any cited references. Since combining the teaching of all of these cited prior art would not arrive at all of the structural elements of the present invention, the objections to Claims 12, 13, 15 and 16 should be withdrawn.

E. Claims 1, 3, 5 - 8, 10, and 11 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Bettle III (Pat. No. 5,320,889) in view of Blinka et al (Pat. No. 5,834,979). The priority date of the present application is May 17, 1995, derived from the foreign applications (Japan) P7-118430 and P7-118430. Verified translations of the priority documents supporting the priority date are attached. Applicants therefore respectfully request withdrawal of this rejection as moot.

F. Claims 1, 3, 5 - 8, 10 and 11 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Bettle III (Pat. No. 5,320,889) in view of JP-0172416 (assigned to Daiichi Seiyaku Co.) and Teumac et al. (Pat. No. 5,663,223). The Examiner indicates that since it is well known that oxygen scavengers can be incorporated in to the layers of polymeric containers, it would be obvious to one skilled in the art to incorporate the oxygen scavenger taught in Daiichi Seiyaku into the ethylene/EVOH blend layer of the laminate taught in Bettle in order to enhance its oxygen barrier properties. Applicants traverse the objection as follows.

Bettle III merely discloses a laminate comprising an EVOH layer. Daiichi Seiyaku merely discloses than an oxygen scavenger comprises a zeolite, either synthetic or natural, which supports one or more ascorbic or araboascorbic acids, their salts or derivatives thereof. The oxygen scavenger is apparently incorporated into the foodstuff that it is protecting. Teumac merely discloses that oxygen scavengers which were once added directly to foodstuff are being incorporated into the food packing container (col. 3, lines 48+). Thus, the cited art does not provide the motivation to combine these elements to arrive at the present invention.

Claims 5 - 8, 10 and 11 ultimately depend upon Claim 1. Claim 1 and 3 are for a resin composition used in a multi-layer laminate with several unique components. None of the cited prior art discloses an A component kneaded into a B component or that both these components undergo changes when the laminate comes into contact with liquid foods. Therefore, the cited art does not provide the motivation to combine these elements to arrive at the present invention. Since combining the teaching of all of these cited prior art would not arrive at all of the structural elements of the present invention, the objections should be withdrawn.

G. Claims 1, 3 and 5-9 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Lofgren et al. (Pat. No. 5,133,999) in view of Blinka et al. (Pat. No. 5, 834,079). The priority date of the present application is May 17, 1995, derived from the foreign applications (Japan) P7-118430 and P7-118430. Verified translations of the priority documents supporting the priority date are attached. Applicants therefore respectfully request withdrawal of this rejection as moot.

H. Claims 1, 3, 4 - 9, 14 and 17 - 19 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Lofgren et al. (Pat. No. 5,133,999) in view of JP-0172416 (assigned to Daiichi Seiyaku Co.) and Teumac et al. (Pat. No. 5,663,223). The Examiner indicates that it would have been obvious to one of ordinary skill in the art to incorporate the oxygen scavenger

taught in Daiichi Seiyaku into the regrind layer of the laminate taught in Lofgren in order to enhance the laminate's oxygen barrier properties. Applicants traverse the objections as follows.

Daiichi Seiyaku merely discloses than an oxygen scavenger comprises a zeolite, either synthetic or natural, which supports one or more ascorbic or araboascorbic acids, their salts or derivatives thereof. The oxygen scavenger is apparently incorporated into the foodstuff that it is protecting. Lofgren merely discloses a layer consisting of a mixture of polyethylene and ethylene vinyl alcohol copolymer (col. 4, lines 61-68). Teumac merely discloses that oxygen scavengers which were once added directly to foodstuff are being incorporated into the food packing container (col. 3, lines 48+). Thus, the cited art does not provide the motivation to combine these elements to arrive at the present invention with its unique and novel advantages.

Claims 4 - 9 ultimately depend upon Claim 1. Claim 1 and 3 are for a resin composition used in a multi-layer laminate with several unique components. None of the cited prior art discloses an A component kneaded into a B component so that component A is protected from oxygen, or that both these components undergo changes when the laminate comes into contact with liquid foods. Thus, the invention is not obvious since combining the cited art would not arrive at all of the structural features of the present application.

Claims 17 - 19 ultimately depend upon Claim 14. Claim 14 has been amended to indicate that the composition is directed to a laminate for packaging aqueous liquid foods. As indicated in the background (page 15 lines 3 - 13), an important feature of the invention is that the laminate for packing aqueous liquid foods comprises a layer made of resin that is prepared by dispersing a porous inorganic compound containing ascorbic acids into hydrophobic thermoplastic resin. The ascorbic acids in the resin layer are stable in the presence of oxygen under dry conditions and normal temperatures. So, it is possible to preserve the above-described function during the storage of the packaging material. However, when filled with aqueous liquid foods, the water component passes through the thermoplastic resin and gradually reaches the supporting

porous inorganic compound, whereby the ascorbic acids exhibit an oxygen absorbing function. Therefore, it becomes possible to prevent any degradation of the liquid foods due to the presence of oxygen during storage. The above mentioned features of Claim 14 are neither disclosed nor suggested in any cited references.

Daiichi Seiyaku discloses porous inorganic compounds containing ascorbic acids. However, Daiichi Seiyaku assumes that ascorbic acids have to be released from porous inorganic compounds to exhibit their oxygen absorbing capability. See attached copy of Japanese and English translation of portions of the same. When the porous inorganic compounds containing ascorbic acids as taught by Daiichi Seiyaku are incorporated in a hydrophobic thermoplastic resin, it is expected that the ascorbic acids would not be released from the porous inorganic compounds. Thus, when the ascorbic acids within the porous inorganic compounds are incorporated in the hydrophobic thermoplastic resin, it is expected that the ascorbic acids would not exhibit any oxygen absorbing capability. Therefore, Applicants believe that another novel feature of the present invention is the incorporation of ascorbic acids into porous inorganic compounds as described on page 13 lines 3 - 18. Since combining the teaching of all of the cited prior art would not arrive at all of the unique aspects of the present invention, the objections should be withdrawn.

I. Claims 1, 3, 5 - 8, 9 - 11, 14 and 17 - 19 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Itamura et al. (Pat. No. 5,13 3,999) in view of JP-0 172416 (assigned to Daiichi Seiyaku Co.) and Teumac: et al. (Pat. No. 5,663,223). The Examiner indicates that it since it is well known that oxygen scavengers can be incorporated into the layer of polymeric container, it would have been obvious to one of ordinary skill in the art to incorporate the oxygen scavenger taught in Daiichi Seiyaku into the ethylene/EVOH layer of the laminate taught in Itamura. in order to enhance the laminate's oxygen barrier properties. Applicants traverse the rejection as follows.

Itamura merely discloses that a composition comprises a polyolefin and a saponified product of ethylene-vinyl acetate copolymer (abstract), in a ratio between 65:35 to 99.7:0.3 (col. 4, lines 61 - 65). The ethylene-vinyl acetate copolymer has a saponification degree of at least 96% (abstract), and the blend may be utilized in laminates (col. 9, lines 1 - 9). Daiichi Seiyaku merely discloses than an oxygen scavenger comprises a zeolite, either synthetic or natural, which supports one or more ascorbic or araboascorbic acids, their salts or derivatives thereof. The oxygen scavenger is apparently incorporated into the foodstuff that it is protecting. Teumac merely discloses that oxygen scavengers which were once added directly to foodstuff are being incorporated into the food packing container (col. 3, lines 48+). Thus, the cited art does not provide the motivation to combine these elements to arrive at the present invention, the unique advantage of which is protection afforded to the organic reducing agent by the hydrophilic water insoluble thermoplastic resin gas barrier.

Claims 5 - 11 ultimately depend upon Claim 1. Claim 1 and 3 are for a resin composition used in a multi-layer laminate with several unique components. None of the cited prior art discloses an A component kneaded into a B component or that both these components undergo changes when the laminate comes into contact with liquid foods. Thus, the invention is not obvious since combining the cited art would not arrive at all of the structural features of the present application.

Claims 17 - 19 ultimately depend upon Claim 14. Claim 14 has been amended to indicate that the composition is directed to a laminate for packaging aqueous liquid foods. As indicated in the background (page 15, lines 3 - 13), an important feature of the invention is that the laminate for packing aqueous liquid foods comprises a layer made of resin that is prepared by dispersing a porous inorganic compound containing ascorbic acids into hydrophobic thermoplastic resin. The ascorbic acids in the resin layer are stable in the presence of oxygen under dry conditions and normal temperatures. So, it is possible to preserve the above-described function

during the storage of the packaging material. However, when filled with aqueous liquid foods, the water component passes through the thermoplastic resin and gradually reaches the supporting porous inorganic compound, whereby the ascorbic acids exhibit an oxygen absorbing function. Therefore, it becomes possible to prevent any degradation of the liquid foods due to the presence of oxygen during storage. The above mentioned features of Claim 14 are neither disclosed nor suggested in any cited references.

Daiichi Seiyaku discloses porous inorganic compounds containing ascorbic acids. However, Daiichi Seiyaku assumes that ascorbic acids have to be released from porous inorganic compounds to exhibit their oxygen absorbing capability. See attached copy of Japanese and English translation of portions of the same. When the porous inorganic compounds containing ascorbic acids as taught by Daiichi Seiyaku are incorporated in a hydrophobic thermoplastic resin, it is expected that the ascorbic acids would not be released from the porous inorganic compounds. Thus, when the ascorbic acids within the porous inorganic compounds is incorporated in the hydrophobic thermoplastic resin, it is expected that the ascorbic acids would not exhibit any oxygen absorbing capability. Therefore, Applicants believe that another novel feature of the present invention is the incorporation of ascorbic acids into porous inorganic compounds as described on page 13, lines 3 - 18. Since combining the teaching of all of the cited prior art would not arrive at all of the compositional elements of the present invention, the objections should be withdrawn.

J. Claims 1, 3, 5 - 8, and 9 - 11 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Itamura et al. (Pat. No. 5,133,999) in view of in view of Blinka et al. (Pat. No. 5, 834,079). The priority date of the present application is May 17, 1995, derived from the foreign applications (Japan) P7-118430 and P7-118430. Verified translations of the priority documents supporting the priority date are attached. Applicants therefore respectfully request withdrawal of this rejection as moot.

K. Claims 2 and 4 were rejected under 35 U.S.C. 103(a) as being unpatentable over any of the above combination of references and further in view of Hofeldt el al. (Pat. No. 5,204,389). The Examiner indicates that since Hofeldt teaches that an effective amount of ascorbate for the purpose of the oxygen scavenging is between 0.5-10wt%, it would have been obvious to one of ordinary skill in the art to utilize such amounts of ascorbate in the above taught laminates. Applicants traverse the objections as follows.

Hofeldt merely discloses a film for a container closure comprising ascorbates or mixtures thereof (col. 5, lines 3 - 7). The amount of scavenger is at least 0.5 wt % based on the polymeric matrix material, and it is generally at least 1% (col. 5, lines 51 - 55). None of the combinations cited above teach that the oxygen scavenger should be contained in amounts raging from 0.05-l0 wt% of the resinous composition. Therefore, the cited art does not provide the motivation to combine these elements to arrive at the present invention.

Claims 2 and 4 depend upon Claims 1 and 3. Claim 1 and 3 are for a resin composition used in a multi-layer laminate with several unique components. None of the cited prior art discloses an A component kneaded into a B component or that both these components undergo changes when the laminate comes into contact with liquid foods. As already indicated above, a person skilled in the art would not be motivated to combine Daiichi Seiyaku with Lofgren, Itamura, Koyama, Teumac or Hofeldt to obtain all of the compositional features of the present invention. Nor does any combination of the references teach the unique and unexpected advantages of the present invention. In any case, the combinations asserted would not be successful in arriving at all of the structural elements of claims 2 and 4. Thus, the rejections should be withdrawn.

No additional fees are believed due; however, the Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 10-1215.

This Response places all claims in the present application in condition for allowance, and such action is courteously solicited. The Examiner is invited and encouraged to contact the undersigned attorney of record if such contact will facilitate an efficient examination and allowance of the application.

Respectfully submitted,

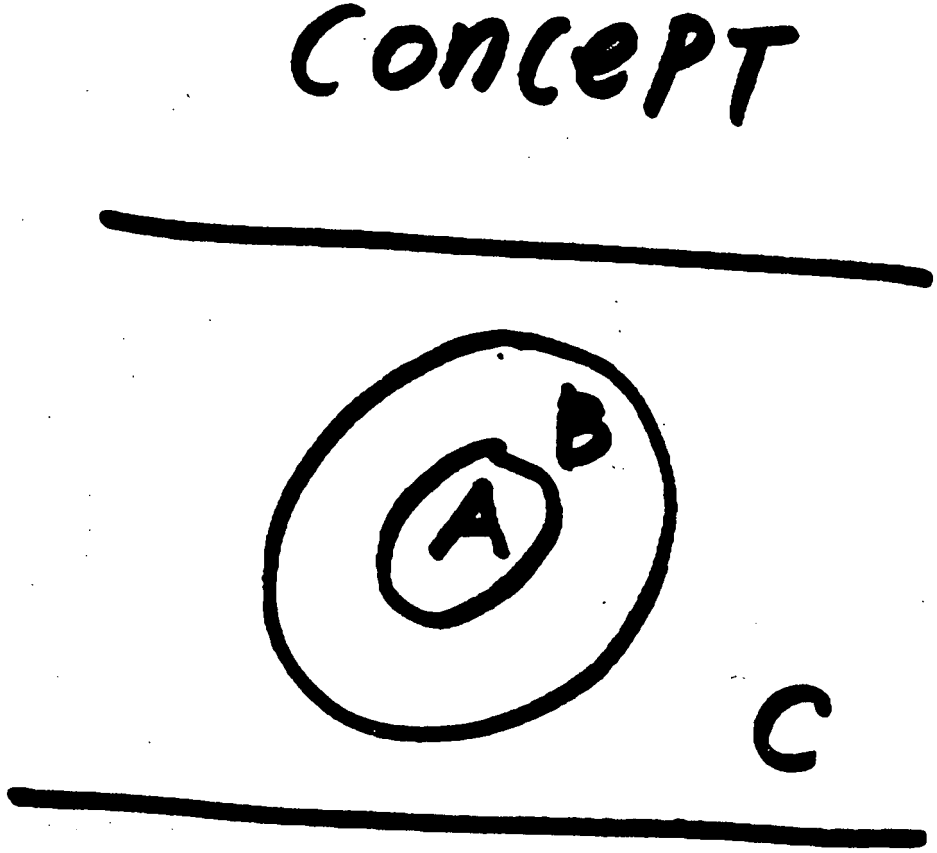
JONES & ASKEW, LLP

By: William L. Warren
Reg. No. 36,714

2400 Monarch Tower
3424 Peachtree Road, N.E.
Atlanta, GA 30326
404-949-2400
Attorney Docket: 13700-0176

Your Ref: 13700-0176
Our Ref: JNTP-27/28-PCT
-U.

Figure A



#11

DECLARATION

I, Masakazu ITO, a citizen of Japan, c/o Miyoshi & Miyoshi of Toranomon Daiichi Bldg., 2-3, Toranomon 1-chome, Minato-ku, Tokyo 105-0001, Japan, do hereby solemnly and sincerely declare:

That I am well acquainted with the Japanese language and English language; and

That the attached is a true and faithful translation made by me of the Japanese document, namely a certified copy of Japanese Patent Application No. 7/118430 to the best of my knowledge and belief.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-captioned application or any patent issuing therefrom.

This 19th day of August, 1999

Masakazu ITO

7-118430

[Name of Document] Patent Application

[Identification Number] NTP-28

[Filing Date] May 17, 1995

[Addressee] Commissioner, Patent Office

[International Patent Classification] B32B 27/00

[Title of Invention] LAMINATE FOR PACKASING LIQUID FOOD

[Number of claim(s)] 4

[Inventor]

[Address] NIHON TETRA PAK, Japan K.K.
2-2-19, Akasaka,
Minato-ku, TOKYO

[Name] Morio HARA

[Inventor]

[Address] NIHON TETRA PAK, Japan K.K.
2-2-19, Akasaka,
Minato-ku, TOKYO

[Name] Norio KOBAYASHI

[Inventor]

[Address] NIHON TETRA PAK, Japan K.K.
2-2-19, Akasaka,
Minato-ku, TOKYO

[Name] Jun TANAKA

[Identification Number] 000229232
[Name] NIHON TETRA PAK, Japan K.K.
[Representative] Claes Du Rietz

[Agent]
[Identification Number] 100105083
[Patent Attorney]
[Name] Yoshitoshi TANAKA

[Agent]
[Identification Number] 100088111
[Patent Attorney]
[Name] Shozo SHIMIZU

[Appointed Agent]
[Identification Number] 100083806
[Patent Attorney]
[Name] Hidekazu MIYOSHI
[Telephone Number] 03-3504-3075
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Appointed Agent]
[Identification Number] 100100712
[Patent Attorney]
[Name] Sachikuni IWASAKI
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Appointed Agent]
[Identification Number] 100095500
[Patent Attorney]
[Name] Masakazu ITO
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Appointed Agent]
[Identification Number] 1000104031
[Patent Attorney]
[Name] Kouichirou TAKAKU
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Indication of Fee]
[Way of Payment] Prepayment
[Prepayment Register Number] 001982
[Ammount of Fee] ¥21,000

[List of Filed Material(s)]
[Name of Material] Specification 1
[Name of Material] Abstract 1
[Number of General Power-of-Attorney] 9401335
[Number of General Power-of-Attorney] 9501043

(NAME OF THE DOCUMENT) SPECIFICATION

(TITLE OF THE INVENTION) LAMINATE FOR PACKAGING LIQUID FOOD

(CLAIM FOR A PATENT)

(Claim 1) A laminate for packaging liquid foods, comprising an innermost layer made of a resin layer that is prepared by dispersing into hydrophobic thermoplastic resin a porous inorganic compound that supports an ascorbic acids.

(Claim 2) A laminate of Claim 1, in which the porous inorganic compound comprises synthetic zeolite.

(Claim 3) A laminate of Claim 1 or 2, in which the hydrophobic thermoplastic resin comprises polyolefin resin.

(Claim 4) A laminate of Claim 3, in which the polyolefin resin comprises polyethylene based resin or polypropylene based resin.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(Field of the Invention)

The present invention relates to a laminate for packaging aqueous liquid food such as juice, milk, liquor and the like.

(0002)

(Prior Art)

Resin containers and paper containers for tightly sealing and packaging liquid food have a wide range of applications because of their adequate strength and lightness.

(0003)

However, the resin containers and paper containers have a higher oxygen permeability than metal cans. Thus, the flavor of the contents sealed and stored therein undergoes degradation, thereby creating problems such as a short quality preservation period of contents.

(0004)

Thus, in order to extend quality preservation period, an oxygen barrier resin such as ethylene-vinyl alcohol copolymer or the like is provided in resin containers. For the paper containers, new containers are created in which a paper base material is laminated by: an aluminum foil; an oxygen barrier resin such as ethylene-vinyl alcohol copolymer, polyvinylden chloride resin or the like; or a resin film on which an inorganic oxide such as silica is deposited. Such containers are used for the storage of liquid food.

(0005)

Further, oxygen absorbing containers have been proposed in which an oxidation catalyst such as cobalt stearate or the like, iron powder and a reducing organic compound is included in the resin layer or adhesive layer that makes up the laminate.

(0006)

However, in the container laminated by the oxygen barrier resin, the blockage of oxygen is not complete. In the container laminated by aluminum foil and resin film on which inorganic oxide is deposited, microscopic cracks (pinholes) can occur during lamination and molding process, to degrade the oxygen gas barrier property.

(0007)

Further, in the case where iron powder is included, the weight of container would increase significantly to obtain a sufficient effect, which makes it impossible to achieve a lightweight container. Moreover, there also exist sanitary problems. In the case where an oxidation catalyst is used, there are problems related to the sanitation and the control of the manifestation of its function.

(0008)

Moreover, in the case where a reducing organic compound is used, difficulty arises such that it is necessary to use a safe compound and care must be taken with regards to the heat resistance and the elution from the resin layer of the organic compound.

(0009)

(Problems to be solved by the Invention)

It is an object of the present invention to provide a resin composition that contains a reducing organic compound and, in the case of packaging liquid foods, can store the content for long period, and to provide a laminate using the resin

resin, polystyrene resin, polyvinyl chloride resin, methacryl resin, ethylene-α-unsaturated carboxylic acid copolymer, ionomer, unsaturated carboxylic acid modified polyolefin, cyclo-olefin copolymer and the like.

(0018)

The polyolefin resin includes polyethylene-based resin (low-density polyethylene, medium-density polyethylene, high-density polyethylene, linear low-density polyethylene, etc.), polypropylene based resin (homopolypropylene, ethylene-propylene random copolymer, ethylene-propylene block copolymer, etc.), polybutene-1, polyhexene-1, polymethylpentene-1 and the like.

(0019)

The ethylene-α-unsaturated carboxylic acid copolymer includes a copolymer comprised of ethylene and an α-unsaturated carboxylic acid such as acrylic acid, methacrylic acid or the like.

(0020)

The unsaturated carboxylic acid modified polyolefin used in the present invention can be obtained by grafting an unsaturated carboxylic acid or derivative thereof to the polyolefin resin described above.

(0021)

The unsaturated carboxylic acid includes α-unsaturated carboxylic acid, α, β-unsaturated dicarboxylic acid, alicyclic unsaturated dicarboxylic acid containing a cis-double bond in a ring and the like. Further, the α-unsaturated carboxylic acid includes acrylic acid, methacrylic acid, crotonic acid and the like. The α, β-unsaturated dicarboxylic acid or the derivative thereof includes maleic acid, maleic acid anhydride and the like. The alicyclic unsaturated dicarboxylic acid containing a cis-double bond in a ring or the derivative thereof includes himic acid, himic acid anhydride, tetrahydrophthalic acid, tetrahydrophthalic acid anhydride, chlorendic acid and the like.

(0022)

The cyclic olefin copolymer is a copolymer of cyclic olefin, and ethylene or α-olefin.

(0023)

Further, the cyclic olefin includes cyclopentene, cyclohexene, cycloheptene, cyclooctene, 2-norbornene and the like, and the α-olefin includes propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and the like.

(0024)

Among the thermoplastic resins described above, polyolefin resins, and

composition.

(0010)

(Means for solving the Problems)

Through intensive research, the present inventors have completed the present invention by finding that the following laminate achieves the object of the present invention. The foregoing laminate is a laminate having an innermost layer of a resin layer made of polyolefin resin and the like that contains a porous inorganic substance supporting an ascorbic acids.

(0011)

That is, according to a gist of the present invention, a laminate for packaging liquid foods comprises an innermost layer made of a resin layer that is prepared by dispersing into hydrophobic thermoplastic resin a porous inorganic compound that supports an ascorbic acids.

(0012)

In this connection, in the laminate of the present invention, the innermost layer refers to the layer that is closest to the liquid foods, namely the layer that is in direct contact with the liquid foods, when the laminate is used to package liquid foods.

(0013)

The ascorbic acids used in the present invention may include ascorbic acid, araboascorbic acid or the salts (sodium salt, potassium salt, etc.) thereof, acyl derivatives (stearoyl and palmitoyl derivatives) and the like.

(0014)

The porous inorganic compounds used in the present invention include zeolite, silica gel, sepiolite, porous silica, porous silica-alumina and the like. Among these, zeolite is particularly preferred.

(0015)

Further, while it is possible to use natural zeolite, synthetic zeolite is preferred in terms of uniformity and purity, with A type, X type and Y type zeolite being particularly preferred. The synthetic zeolite may be a hydrogen type or cation type (sodium type, potassium type, calcium type, etc.) zeolite.

(0016)

In this connection, these porous inorganic compounds are preferably dried before being used.

(0017)

As for a hydrophobic thermoplastic resin, it is possible to use polyolefin

in particular polyethylene based resins and polypropylene-based resins are preferred.

(0025)

With regards to the method of making the porous inorganic compound supporting the ascorbic acids, it is possible to employ a method in which both compounds are brought into contact inside an appropriate medium. In this connection, appropriate mediums include alcohols, ethers, ketones, hydrocarbons, halohydrocarbons and the like.

(0026)

A preferred method is as follows. That is, the porous inorganic compound may be immersed into a lower alcohol solution of ascorbic acids, such as an ethanol solution of ascorbic acids. Or the solution is passed through a column filled with the porous inorganic compound. Thus, the solution is absorbed by the porous inorganic compound. Such methods may also be carried out under heated conditions.

(0027)

The ascorbic acids and porous inorganic compound is used in the ratio that the weight of the porous inorganic compound is 1 ~ 50 times greater than that of the ascorbic acids, and in particular in the ratio that the former is 1.2 ~ 10 times greater than that of the latter.

(0028)

In the method of dispersing the porous inorganic compound that supports an ascorbic acids as described above (that compound is hereinafter referred to a supporting porous inorganic compound) into the hydrophobic thermoplastic resin, it is preferred that both compounds are kneaded at a temperature not lower than the melting temperature of the thermoplastic resin by means of an appropriate kneading machine, particularly preferably an extruder.

(0029)

It is not possible to establish an absolute usage ratio of the supporting porous inorganic compound and thermoplastic resin because it depends on the type of liquid foods, the storage period and the environmental conditions existing inside and outside the storage container. However, during the kneading of both compounds, the supporting porous inorganic compound should normally be present in the range of 2 ~ 50% by weight, and preferably in the range of 5 ~ 30% by weight.

(0030)

These proportions are for the resin layer that will form the innermost layer of the laminate of the present invention. Thus, it is possible to prepare in advance a master batch in which contents of the supporting porous inorganic compound have a ratio that exceeds the above-described ratio, and dilute an appropriate portion thereof with the thermoplastic resin so as to realize the above-described ratio, when forming the laminate.

(0031)

The laminate of the present invention can be constructed by forming the innermost layer from a resin layer made of the above-described kneaded compounds. As for the base material layer of the laminate, it is possible to use any base material normally used in packaging of liquid foods, such as films and sheets made of various synthetic resins, paper, metal foil and the like or a laminate comprised of such materials.

(0032)

Further, there is no limitation to the method of laminating the base material layer with the above-described resin layer, and it is possible to use standard lamination methods.

(0033)

For example, it is possible to use: an extrusion lamination method in which the resin layer undergoes an extrusion, coating onto the base material layer; a dry lamination method in which a film or sheet resin layer is laminated onto the base material layer with adhesives or the like placed therebetween; a direct lamination method in which at least a surface of the base material layer, or the film or sheet resin layer is melted to laminate the two layers together; a so-called sandwich lamination method in which the base material layer and the film or sheet resin layer are laminated with an intermediate layer constituting a adhesive layer extruded therebetween; and a coextrusion-lamination method in which a synthetic resin that forms the base material and a resinous kneaded compound that forms the resin layer are extruded from a flat die or circular die mounted in an extruder and the like, so that the both are laminated with each other.

(0034)

In the laminate of the present invention, as described above, the basic layer may be made from the base material layer and the above-described resin layer. However, a layer or layers made of the same material or a different material (e.g., a gas-barrier resin layer, an inorganic compound vapor deposited resin film, etc.)

may be provided between the base material layer and the above-described resin layer or on the outside of the base material layer, to construct a multilayered laminate.

(0035)

A container for storing liquid foods formed from the laminate of the present invention having the above-described construction exhibits an oxygen absorbing function when the water content of the liquid foods filled in the container acts on the innermost layer.

(0036)

That is, because the ascorbic acids in the resin layer is stable in the presence of oxygen under dry conditions at normal temperatures, the capability of the ascorbic acids thereof is maintained during the storing of the packaging material. However, when the packaging is filled with contents, the water content passes through the thermoplastic resin and gradually reaches the supporting porous inorganic compound, whereby the ascorbic acid exhibits an oxygen absorbing function.

(0037)

(Preferred Embodiments)

Hereinafter, various embodiments of the present invention will be explained in detail.

(0038)

(Embodiment)

A solution of warm ethanol 7.21 having 300g of ascorbic acid dissolved therein was slowly passed through a glass column filled with 500g of A type zeolite to cause the zeolite to support the ascorbic acid. Then, after washing this supporting zeolite with chilled ethanol, drying was carried out at reduced pressure to prepare ascorbic acid supporting zeolite.

(0039)

Next, 30 parts by weight of this zeolite thus obtained and supporting ascorbic acid and 70 parts by weight of low-density polyethylene (having density of 0.919g/cm3) (LDPE) were supplied to a dual extruder and kneaded to obtain a master batch in which the content of the ascorbic acid supporting zeolite is 30% by weight.

(0040)

Then, to lower the ascorbic acid supporting zeolite content to 10% by weight, this master batch and the LDPE described above and ethylene-acrylic

acid copolymer (having density of 0.94g/cm3) (EAA) were supplied respectively to an extruder. Then, they are coextruded from the circular die of the extruder to form a two-layer inflation film comprised of a 30μm supporting zeolite containing LDPE layer and a 10μm EAA layer.

(0041)

Next, this two-layer inflation film and a base material comprised of LDPE (15μm)-paperboard (having basis weight of 200g/m2)-LDPE (15μm)-aluminum foil (7μm) underwent sandwich lamination at 280℃using a adhesion layer of EAA (20μm). Then, a laminate of the present invention having the structure indicated below is obtained.

(0042)

LDPE-paperboard-LDPE-aluminum foil//EAA//EAA-supporting zeolite containing LDPE.

Using this laminate, a brick-shaped paper container was obtained so that the supporting zeolite containing LDPE layer was used for the inside surface of the container. A paper container filling machine filled the container with 250ml of deaerated water having a dissolved oxygen concentration of 0.5mg/l.

(0043)

This container filled with deaerated water was then placed into a constant temperature bath at 37℃and kept there for a prescribed period of time, during which the concentration of dissolved oxygen in the deaerated water was measured. The results of such measurements are shown in Table 1.

(0044)

(Comparative Example 1)

Except for using A type zeolite that does not support ascorbic acid, a laminate was constructed in the same manner as described for the foregoing embodiment. Then, the laminate underwent the same evaluation as was carried out for embodiment.

(0045)

The results of evaluation are shown in Table 1.

(0046)

(Comparative Example 2)

Except for not using ascorbic acid containing zeolite, a laminate was constructed in the same manner as described for the embodiment. And the laminate underwent the same evaluation as was carried out for embodiment. The results are the same as those of Comparative Example 1.

(0047)

(Table 1)

Storage Period	Concentration of Dissolved Oxygen (mg/l) Directly after Filling	7 days	14 days	28 days
Embodiment	0.5	1.1	1.3	1.8
Comparative Example 1	0.5	1.3	2.0	3.1

(0048)

(EFFECTS OF THE INVENTION)

Because the laminate of the present invention absorbs and reduces oxygen permeated through the base material layer, it is possible to suppress degradation due to oxygen of liquid foods packaged by the laminate and maintain quality of the liquid foods and extend quality preservation period.

(0049)

Further, it is easy to adjust the oxygen absorbing capability by changing the concentration of the ascorbic acids supported by the porous inorganic compound or the additive amount of the supporting porous inorganic compound. Thus, it is simple to carry out the adjustment in accordance with the type of liquid foods and the internal and external environmental conditions present during storing of such foods.

(NAME OF THE DOCUMENT) ABSTRACT

(ABSTRACT)

(PURPOSE) To provide a laminate for packaging aqueous liquid foods, which can prevent degradation thereof due to oxygen from the inside and outside, and can preserve contents thereof safely for a long period.

(CONSTITUTION) The present invention teaches a laminate having an innermost layer of a hydrophobic thermoplastic resin layer in which a porous inorganic compound supporting ascorbic acids is dispersed.

(SELECTED FIGURE) None

DECLARATION

I, Masakazu ITO, a citizen of Japan, c/o Miyoshi & Miyoshi of Toranomon Daiichi Bldg., 2-3, Toranomon 1-chome, Minato-ku, Tokyo 105-0001, Japan, do hereby solemnly and sincerely declare:

That I am well acquainted with the Japanese language and English language; and

That the attached is a true and faithful translation made by me of the Japanese document, namely a certified copy of Japanese Patent Application No. 7/118426 to the best of my knowledge and belief.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further, that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-captioned application or any patent issuing therefrom.

This 19th day of August, 1999

Masakazu ITO

7-118426

[Name of Document] Patent Application

[Identification Number] NTP-27

[Filing Date] May 17, 1995

[Addressee] Commissioner, Patent Office

[International Patent Classification] C08L 23/02
B32B 27/00

[Title of Invention] RESIN COMPOSITION FOR STORAGE OF LIQUID FOOD, AND LAMINATE USING THE SAME

[Number of claim(s)] 7

[Inventor]

[Address] NIHON TETRA PAK, Japan K.K.
2-2-19, Akasaka,
Minato-ku, TOKYO

[Name] Morio HARA

[Inventor]

[Address] NIHON TETRA PAK, Japan K.K.
2-2-19, Akasaka,
Minato-ku, TOKYO

[Name] Norio KOBAYASHI

[Inventor]

[Address] NIHON TETRA PAK, Japan K.K.
2-2-19, Akasaka,
Minato-ku, TOKYO

[Name] Jun TANAKA

[Identification Number] 000229232
[Name] NIHON TETRA PAK, Japan K.K.
[Representative] Claes Du Rietz

[Agent]
[Identification Number] 100105083
[Patent Attorney]
[Name] Yoshitoshi TANAKA

[Agent]
[Identification Number] 100088111
[Patent Attorney]
[Name] Shozo SHIMIZU

[Appointed Agent]
[Identification Number] 100083806
[Patent Attorney]
[Name] Hidekazu MIYOSHI
[Telephone Number] 03-3504-3075
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Appointed Agent]
[Identification Number] 100100712
[Patent Attorney]
[Name] Sachikuni IWASAKI
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Appointed Agent]
[Identification Number] 100095500
[Patent Attorney]
[Name] Masakazu ITO
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Appointed Agent]
[Identification Number] 1000104031
[Patent Attorney]
[Name] Kouichirou TAKAKU
[Particular Statement for Subagent] Subagent of Applicant; NIHON TETRA PAK, Japan K.K.

[Indication of Fee]
[Way of Payment] Prepayment
[Prepayment Register Number] 001982
[Ammount of Fee] ¥21,000

[List of Filed Material(s)]
[Name of Material] Specification 1
[Name of Material] Abstract 1
[Number of General Power-of-Attorney] 9401335
[Number of General Power-of-Attorney] 9501043

NTP 77

(NAME OF THE DOCUMENT) SPECIFICATION

(TITLE OF THE INVENTION) RESIN COMPOSITION AND LAMINATE FOR STORAGE OF LIQUID FOOD

(CLAIM FOR A PATENT)

(Claim 1) A resin composition for storing liquid foods, in which a hydrophilic reducing organic compound is coated with a hydrophilic and water insoluble thermoplastic resin and is dispersed in a hydrophobic thermoplastic resin.

(Claim 2) A composition as claimed in Claim 1, in which the hydrophilic reducing organic compound is a compound selected from ascorbic acids, polyphenols and catechins.

(Claim 3) A composition as claimed in Claim 1 or 2, in which the hydrophilic and water insoluble thermoplastic resin is ethylene-vinyl alcohol copolymer, polyvinyl alcohol having a saponification degree of 95% or higher, or polyamide resin.

(Claim 4) A composition as claimed in any one of Claims 1 to 3, in which the hydrophobic thermoplastic resin comprises polyolefin resin.

(Claim 5) A composition as claimed in any one of Claims 1 to 4, in which the hydrophilic reducing organic compound is present in the range of 0.05 ~ 10% by weight, and the hydrophilic and water insoluble thermoplastic resin is present in the range of 3 ~ 40% by weight.

(Claim 6) A laminate for packaging liquid foods comprising an innermost layer made of the composition claimed in any one of Claims 1 to 5.

(Claim 7) A laminate for packaging liquid foods comprising an innermost layer made of a hydrophilic and water insoluble thermoplastic resin and a layer adjacent to the innermost layer made of the composition claimed in any one of Claims 1 to 5.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001)

(Field of the Invention)

The present invention relates to a resin composition and a laminate for storage of aqueous liquid food such as juice, milk, liquor and the like.

(0002)

(Prior Art)

Resin containers and paper containers for tightly sealed packaging of liquid food have a wide range of applications because of their adequate strength and lightness.

(0003)

However, because resin containers and paper containers have a higher oxygen permeability than metal cans, the flavor of the contents sealed and stored therein undergoes degradation, thereby creating problems such as a short quality preservation period of contents and the like.

(0004)

Thus, in order to extend quality preservation period, an oxygen barrier resin such as ethylene-vinyl alcohol copolymer or the like is provided in resin containers. For the paper containers, new containers are created in which a paper base material is laminated by: an aluminum foil; an oxygen barrier resin such as ethylene-vinyl alcohol copolymer, polyvinylden chloride resin or the like; or a resin film on which an inorganic oxide such as silica is deposited. Such containers are used for the storage of liquid food.

(0005)

Further, oxygen absorbing containers have been proposed in which an oxidation catalyst such as cobalt stearate or the like, iron powder and a reducing organic compound is included in the resin layer or adhesive layer that makes up the laminate.

(0006)

However, in the container laminated by the oxygen barrier resin, the blockage of oxygen is not complete. In the container laminated by aluminum foil and resin film on which inorganic oxide is deposited, microscopic cracks (pinholes) can occur during lamination and molding process, to degrade the oxygen gas barrier property.

(0007)

Further, in the case where iron powder is included, the weight of container would increase significantly to obtain sufficient effect, which makes it impossible to achieve a lightweight container. Moreover, there also exist sanitary problems. In the case where an oxidation catalyst is used, there are problems related to the sanitation and the control of the manifestation of its function.

(0008)

Moreover, in the case where a reducing organic compound is used, difficulty arises such that it is necessary to use a safe compound and care must be taken with regards to the heat resistance and the elution from the resin layer of the organic compound.

(0009)

(Problems to be solved by the Invention)

It is an object of the present invention to provide a resin composition that contains a reducing organic compound and that make it possible to safely package and store contents of liquid food for a long period, and to provide a laminate using such resin composition.

(0010)

(Means for Solving the Problems)

Through intensive research, the present inventors were able to complete the present invention by finding that the following resin composition and laminate achieve the object of the present invention. The foregoing resin composition and a laminate comprising the composition are obtained by dispersing beforehand a hydrophilic reducing organic compound into a hydrophilic and water insoluble thermoplastic resin to coat its surface therewith, and then by dispersing the resulted material in a hydrophobic thermoplastic resin while holding the coatings. The laminate is constructed so that the innermost layer is made of the foregoing composition, or that the innermost layer is made of a specific resin with the layer adjacent to the innermost layer being the layer comprising the foregoing composition.

(0011)

That is, the gist of the present invention is: (1) the resin composition for storing liquid foods, in which a hydrophilic reducing organic compound is coated with a hydrophilic and water insoluble thermoplastic resin and is dispersed in a hydrophobic thermoplastic resin; (2) the laminate for packaging liquid foods comprising an innermost layer made of the layer comprising the composition of (1) described above; and (3) the laminate comprising an innermost layer made of a hydrophilic and water insoluble thermoplastic resin and a layer adjacent to the innermost layer made of the composition of (1) described above.

(0012)

In this connection, in the laminate of the present invention, the innermost layer refers to the layer that is closest to the liquid foods, namely the layer that is in direct contact with the liquid foods, when the laminate is used for package liquid foods.

(0013)

The hydrophilic reducing organic compound in accordance with the present invention may include an ascorbic acids, a polyphenols, a catechins or the like,

and the ascorbic acids may include ascorbic acid, araboascorbic acid or the salts (sodium salt, potassium salt, etc.) thereof and the like.

(0014)

The polyphenols includes pyrogallol, catechol, gallic acid, resorcin, hydroquinone, and it is possible to use any mixture thereof.

(0015)

The catechins include epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate, and it is possible to use any mixture thereof.

(0016)

Among these reducing organic compounds, the ascorbic acids and the catechins are preferred, with ascorbic acid being particularly preferred.

(0017)

With regards to a hydrophilic and water insoluble thermoplastic resin, it is possible to use ethylene-vinyl alcohol copolymer, polyvinyl alcohol having a saponification degree of 95% or higher, polyamide resin (nylon 6, nylon 66, nylon 11, etc.), acetyl cellulose and the like. Among these, ethylene-vinyl alcohol copolymer is particularly preferred.

(0018)

As for a hydrophobic thermoplastic resin, it is possible to use polyolefin resin, polystyrene resin, polyvinyl chloride resin, methacryl resin, ethylene-α-unsaturated carboxylic acid copolymer, ionomer, unsaturated carboxylic acid modified polyolefin, cyclo-olefin copolymer and the like.

(0019)

The polyolefin resin includes polyethylene-based resin (low-density polyethylene, medium-density polyethylene, high-density polyethylene, linear low-density polyethylene, etc.), polypropylene based resin (homopolypropylene, ethylene-propylene random copolymer, ethylene-propylene block copolymer, etc.), polybutene-1, polyhexene-1, polymethylpentene-1 and the like.

(0020)

The ethylene- α -unsaturated carboxylic acid copolymer includes a copolymer comprised of ethylene and an α -unsaturated carboxylic acid such as acrylic acid, methacrylic acid or the like.

(0021)

The unsaturated carboxylic acid modified polyolefin used in the present invention can be obtained by grafting an unsaturated carboxylic acid or derivative thereof to the polyolefin resin described above.

(0022)

The unsaturated carboxylic acid includes α -unsaturated carboxylic acid, α, β -unsaturated dicarboxylic acid, alicyclic unsaturated dicarboxylic acid containing a cis-double bond in a ring and the like. Further, the α -unsaturated carboxylic acid includes acrylic acid, methacrylic acid, crotonic acid and the like. The α, β-unsaturated dicarboxylic acid or the derivative thereof includes maleic acid, maleic acid anhydride and the like. The alicyclic unsaturated dicarboxylic acid containing a cis-double bond in a ring or the derivative thereof includes himic acid, himic acid anhydride, tetrahydrophthalic acid, tetrahydrophthalic acid anhydride, chlorendic acid and the like.

(0023)

The cyclic olefin copolymer is a copolymer of cyclic olefin, and ethylene or α -olefin.

(0024)

Further, the cyclic olefin includes cyclopentene, cyclohexene, cycloheptene, cyclooctene, 2-norbornene and the like, and the α -olefin includes propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and the like.

(0025)

Among the thermoplastic resins described above, polyolefin resins, and in particular polyethylene based resins and polypropylene-based resins are preferred.

(0026)

The composition of the present invention includes the hydrophilic reducing organic compound (hereinafter, referred to as the "A component") coated with the hydrophilic and water insoluble thermoplastic resin (hereinafter, referred to as the "B component") and dispersed in a hydrophobic thermoplastic resin (hereinafter, referred to as the "C component"). The composition is prepared as follows. After first kneading the A component and the B component, a surface of the A component is coated with the B component, and then these components are then kneaded with the C component for preparation.

(0027)

The kneading of the A component and the B component are preferably carried out at a temperature not higher than the melting point or decomposition point of the A component and not lower than the melting temperature of the B component by an appropriate kneading machine, and in particular preferably by an extruder.

(0028)

Although it is not possible to establish an absolute usage ratio of the A component and the B component because of its dependence on the type of A component and B component, the type of liquid foods, the storage period and the environmental conditions existing inside and outside the storage container, during the kneading of the A component and the B component, the A component should normally be present in the range of 0.1 ~ 50% by weight, and preferably in the range of 0.2 ~ 20% by weight.

(0029)

Next, the kneaded compound comprised of the A component and the B component obtained as described above is kneaded with and dispersed in the C component under condition that a surface of the A component is coated with the B component, to obtain the composition of the present invention. The kneading of the kneaded component and the C component is preferably carried out at a

temperature not lower than the melting temperature of the C component in the same manner as the kneading of the A component and B component.

(0030)

For the same reason as was explained above for the case of kneading the A component and the B component, it is not possible to establish an absolute kneading ratio between the C component and the kneaded compound comprised of the A component and the B component, but in general in the composition of the present invention, the A component should normally be present in the range of 0.5 ~ 10% by weight and preferably in the range of 0.2 ~ 5% by weight, the B component should normally be present in the range of 3 ~ 40% by weight and preferably in the range of 5 ~ 30% by weight. The C component should preferably be present in the residue.

(0031)

When necessary, it is possible to use a compatibilizer such as maleic acid anhydride modified polyolefin or the like when kneading the C component and the kneaded compound comprised of the A component and the B component.

(0032)

The compositions of the present invention obtained as described above can be used as a packaging material for storing liquid foods, or they can be used while mixing with a raw material for making such a packing material.

(0033)

Further, the compositions can be molded into an appropriately shaped molded body, which can be put into liquid contents. Or the shaped molded body rapped by an appropriate member can be put into liquid contents.

(0034)

The present invention includes a laminate for packaging liquid food, in which the innermost layer is made from the foregoing compositions, and a laminate in which the innermost layer is made from the hydrophilic and water insoluble thermoplastic resin with an adjacent layer to the innermost layer being

made from the foregoing compositions. In this connection, as for the hydrophilic and water insoluble thermoplastic resin used for the innermost layer, it is possible to select any of the compounds from the B component which makes up one component of the foregoing compositions, and particularly, ethylene-vinyl alcohol copolymer is preferred.

(0035)

As for the base material layer of the laminate, it is possible to use any base material normally used in packaging of liquid foods, such as films and sheets made of various synthetic resins, paper, metal foil and the like or a laminate comprised of such materials.

(0036)

Further, there is no limitation to the method of laminating the base material layer with the layer comprised of the foregoing composition (which may be hereafter referred to as the resin layer), and it is possible to use standard lamination methods.

(0037)

For example, it is possible to use: an extrusion lamination method in which the resin layer undergoes an extrusion, coating onto the base material layer; a dry lamination method in which a film or sheet resin layer is laminated onto the base material layer with adhesives or the like placed therebetween; a direct lamination method in which at least a surface of the base material layer, or the film or sheet resin layer is melted to laminate the two layers together; a so-called sandwich lamination method in which the base material layer and the film or sheet resin layer are laminated with an intermediate layer constituting a adhesive layer extruded therebetween; and a coextrusion-lamination method in which a synthetic resin that forms the base material and a resinous kneaded compound that forms the resin layer are extruded from a flat die or circular die mounted in an extruder and the like, so that the both are laminated with each other.

(0038)

Further, the method of laminating the innermost layer comprised of the hydrophilic and water insoluble thermoplastic resin and the adjacent layer comprised of the above-described resin layer may be similar to the method of laminating the base material layer and the resin layer.

(0039)

In the laminate of the present invention, as described above, the basic layer may be made from the base material layer and the above-described resin layer. However, a layer or layers made of the same material or a different material (e.g., a gas-barrier resin layer, an inorganic compound vapor deposited resin film, etc.) may be provided between the base material layer and the above-described resin layer or on the outside of the base material layer, to construct a multilayered laminate.

(0040)

A container for storing liquid foods formed from the foregoing composition (which includes packaging materials, formed material, and the like made therefrom) and the laminate having the above-described construction exhibit an oxygen absorbing function when the water content of the liquid foods filled and sealed inside the container acts on the composition, innermost layer or the layer adjacent to the innermost layer.

(0041)

Namely, before the contents being filled, the A component is coated with the B component that has an oxygen gas barrier characteristics and is prevented from being consumed by surrounding oxygen, so that it maintains its oxygen absorbing capability. However, when the contents are filled, the water component gradually reaches, through the C component, the B component dispersed in the C component, which causes the B component to lose its oxygen barrier characteristics, whereby the A component included therein exhibits an oxygen absorbing function.

(0042)

(Embodiments)

Hereinafter, various embodiments of the present invention will be explained in detail.

(0043)

(Embodiment 1)

Five parts by weight of ascorbic acid and 95 parts by weight of ethylene-vinyl alcohol copolymer (containing ethylene at 47 molar %, with a melting temperature of 160℃) was supplied to a dual extruder and kneaded, with both substances then being output from the die of the extruder in the form of a pellet.

(0044)

Next, 10 parts by weight of the above-described pellet and 90 parts by weight of low-density polyethylene (with density of 0.919g/cm3) were kneaded in the same manner as described above to obtain a pellet of the composition of the present invention having an ascorbic acid content of 0.5% by weight.

(0045)

Then, 50g of this pellet and 10ml of distilled water were placed in a 180ml-volume, oxygen-impermeable, cup-shaped container which was then sealed by heat sealing with an oxygen-impermeable film.

(0046)

Next, this container was placed in a constant temperature bath at 15℃ and the concentration of oxygen was measured with an oxygen microanalyzer directly after the heat sealing, after one week and then after two weeks to determine the reduction in the oxygen content, thereby giving the amounts of oxygen absorbed. These absorbed amounts of oxygen are shown in Table 1.

(0047)

(Embodiment 2)

Except for using 20 parts by weight of a kneaded compound comprised of ascorbic acid and ethylene-vinyl alcohol copolymer and 80 parts by weight of low-density polyethylene, the process carried out in this example embodiment was the

same as that of Embodiment 1, whereby a pellet of the composition having an ascorbic acid content of 1% by weight was obtained.

(0048)

Using this pellet, the same oxygen absorbing analysis as described in Embodiment 1 was carried out, and the results thereof are shown in Table 1.

(0049)

(Embodiment 3)

Except for using a pellet made of 10 parts by weight of ascorbic acid and 90 parts by weight of ethylene-vinyl alcohol copolymer, the process carried out in this example embodiment was the same as that of Embodiment 2, whereby a pellet of the composition of the present invention having an ascorbic acid content of 2% by weight was obtained.

(0050)

Using this pellet, the same oxygen absorbing analysis described in Embodiment 1 was carried out, and the results thereof are shown in Table 1.

(0051)

(Comparative Example 1)

Except for not using ascorbic acid, the process carried out in this comparative example was the same as that of Embodiment 1, and using the thus-obtained pellet, the same oxygen absorbing analysis described in Embodiment 1 was carried out, with the results thereof being shown in Table 1.

(0052)

(Reference Examples 1 ~3)

Except for not using distilled water, the pellets comprised of the compositions of the present invention obtained in Embodiments 1 ~ 4 were subjected to the same sealing, storage and oxygen absorbing analysis as that carried out in Embodiment 1, with the results thereof being shown in Table 1. In this regard, Reference Example 1 corresponds to Embodiment 1, Reference

Example 2 corresponds to Embodiment 2, and Reference Example 3 corresponds to Embodiment 3.

(0053)

(Table 1)

	Amounts of Oxygen Absorbed (ml)		
	Directly after Heat Sealing	After One Week	After Two Weeks
Embodiment 1	0.0	0.7	1.3
Embodiment 2	0.0	1.1	2.0
Embodiment 3	0.0	2.8	5.2
Comparative Example 1	0.0	0.0	0.0
Reference Example 1	0.0	0.0	0.0
Reference Example 2	0.0	0.0	0.0
Reference Example 3	0.0	0.0	0.1

(0054)

(EFFECTS OF THE INVENTION)

Because the composition of the present invention exhibits an oxygen absorbing function in the presence of water, when a container is formed from the laminate which includes an innermost layer containing the composition, it is possible to absorb not only the oxygen enclosed inside such container, but also oxygen which passes through from the outside of such container, thereby making it possible to reduce the amount of oxygen present.

(0055)

Accordingly, it becomes possible to prevent degradation of the liquid foods due to oxygen during storage, whereby it becomes possible to preserve the quality and extend the shelf life thereof.

(0056)

Further, it is easy to adjust the oxygen absorbing capability by changing the concentration of the reducing organic compound, and the kneaded compound mixing proportion of the reducing organic compound and the hydrophilic and water insoluble thermoplastic resin. Accordingly, it is simple to carry out adjustment to correspond with the type of foods to be preserved and the internal and external environmental conditions present during storage of such foods.

(NAME OF THE DOCUMENT) ABSTRACT

(ABSTRACT)

(PURPOSE) To provide a raw material suitable for a packaging material etc. for aqueous liquid foods, which can preserve contents safely for a long time by suppressing degradation due to oxygen; and to provide a foods packaging laminate using it.

(CONSTITUTION) The present invention teaches a composition in which a hydrophilic reducing organic compound is dispersed in a hydrophobic thermoplastic resin by means of a hydrophilic and water insoluble thermoplastic resin, and a laminate having an innermost layer made of such composition.

(SELECTED FIGURE) None